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Final Report | November 27, 1962 to December 31, 1963

HEAT RESISTANT HYDRAULIC FLUIDS

Prepared for:

BUREAU OF SHIPS
DEPARTMENT OF THE NAVY
WASHINGTON, D.C.
ATTN: CODE 634A

CONTRACT NOs 88248 ✓
PROJECT SERIAL NO. SR001-03-01
TASK 0606

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA

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CONTENTS

LIST OF TABLES	iii
INTRODUCTION	1
SUMMARY	3
PHYSICAL PROPERTIES OF C-5 AND C-7 FLUOROALCOHL CARBONATES AND ORTHOCARBONATES	4
SYNTHESIS OF FLUOROALCOHOL ORTHOCARBONATES AND CARBONATES	7
Orthocarbonate Formation	7
Proof of Structure	9
Bis Carbonate Formation	10
MISCELLANEOUS REACTIONS	12
EXPERIMENTAL	13
1H, 1H, 7H-Dodecafluoroheptyl Orthocarbonate	15
1H, 1H, 7H-Dodecafluoroheptyl Orthoformate	15
1H, 1H, 7H-Dodecafluoroheptyl Orthobenzoate	16
1H, 1H, 5H-Octafluoropentyl Chlorocarbonate	16
1H, 1H, 5H-Octafluoropentyl -- 1H, 1H, 7H-Dodecafluoroheptyl Carbonate	17
ACKNOWLEDGMENTS	17

TABLES

Table I	1
Table II	4
Table III	Stability-Corrosivity Data on Fluoroalcohol Carbonates and Orthocarbonates	5
Table IV	Fluoroalcohol Orthoesters and Carbonates	13
Table V	Nuclear Magnetic Resonance Data on Orthoesters	14

INTRODUCTION

Current hydraulic fluids are often unacceptable for some applications in forthcoming advanced military weapons. Either they are thermally too unstable for operation at the temperatures expected, or, if thermally stable, they may be deficient in other properties. Many fluids fail at low temperatures because of insufficient fluidity, or fail at high temperatures because of excessive volatility and instability to moisture and oxidation. The increasing complexity of hydraulic systems operating under extreme conditions present the even more serious hazard of hydraulic fires or explosions in various military applications. Consequently, flammability is a serious deficiency inherent in the structure of many otherwise usable compounds.

During an in-house investigation at Stanford Research Institute it was found that the fluorinated alcohols, $\text{H}(\text{CF}_2)_4, _6\text{CH}_2\text{OH}$, would react with polyhalomethanes by a new ferric chloride-catalyzed reaction to give the orthocarbonates and the normal bis carbonates (Table I). The high boiling point and oily characteristics of the octafluoropentyl orthocarbonate stimulated an interest in whether this class of compounds might have certain properties desired of a fluid or lubricant for use at elevated temperatures. The results of the preliminary tests on an impure sample revealed fire resistance, hydrolytic stability, and low pour point.

Table I

Compound	B. P.
Octafluoropentyl (C-5)	
Carbonate $\text{H}(\text{CF}_2)_4\text{CH}_2\text{O})_2\text{C}=\text{O}$	98°/0.005 mm
Orthocarbonate $\text{H}(\text{CF}_2)_4\text{CH}_2\text{O})_4$	135°/0.003 mm
Dodecafluoroheptyl (C-7)	
Carbonate $\text{H}(\text{CF}_2)_6\text{CH}_2\text{O})_2\text{C}=\text{O}$	99°/0.01 mm
Orthocarbonate $\text{H}(\text{CF}_2)_6\text{CH}_2\text{O})_4\text{C}$	170°/0.008 mm

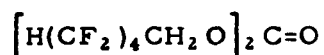
These new classes of fluids have not been evaluated previously; on the basis of the preliminary tests, they appeared to possess better fire resistance characteristics and other properties than many current materials. The properties related to lubrication and hydraulic applications had not been determined. However, since some of these compounds approach being fireproof, it was desirable to evaluate them as base fluids or as additives to increase the fire resistance of fluids now in use.

~~Consequently, under the sponsorship of the Navy Bureau of Ships,~~
Stanford Research Institute has been carrying on a program in the synthesis^{and} and evaluation^{of} ~~of the~~ fluoroalcohol orthocarbonates and bis carbonates as fire-resistant fluids. ~~Because the method for synthesis of the compounds was not optimum,~~ a large part of the effort was concerned with a study of the preparation of the orthocarbonates and bis carbonates. Preliminary evaluation was done on a laboratory scale of ~~such~~ physical properties^{as} as viscosity, corrosivity, hydrolytic stability, flash point, fire point, and density. ~~In addition,~~ two quarts each of bis (octafluoropentyl) carbonate, octafluoropentyl orthocarbonate, and bis (dodecafluoroheptyl) carbonate, one quart of dodecafluoroheptyl orthocarbonate, and 100 milliliters of dodecafluoroheptyl orthobenzoate were prepared ~~and submitted to the Marine Engineering Laboratory for evaluation.~~ ~~Because evaluation of these compounds was not encouraging, the project is not being continued.~~

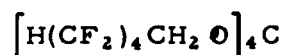
This Final Report summarizes our work on the physical properties of the fluoroalcohol carbonates and orthocarbonates, and on the determination of optimum conditions for the synthesis of the compounds.

SUMMARY

Under the sponsorship of the Navy Bureau of Ships, Stanford Research Institute carried out a program on the synthesis and preliminary evaluation of several fluoroalcohol orthocarbonates and bis carbonates (cpds I-IV) as fire-resistant fluids. Physical property tests revealed that the compounds were hydrolytically stable, were not corrosive to copper, and would not support a flame. The specific gravity of each of the materials was unusually high (> 1.60 gm/ml).



Octafluoropentyl Carbonate, I

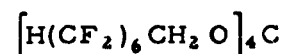


Octafluoropentyl Orthocarbonate, II



Dodecafluoroheptyl Carbonate,

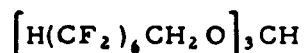
III



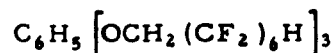
Dodecafluoroheptyl Orthocarbonate,

IV

Optimum conditions for the synthesis of the compounds were developed. The orthocarbonates were prepared by the ferric chloride-catalyzed reaction of carbon tetrachloride with fluoroalcohols in either chloroform or carbon tetrachloride as solvent. The bis carbonate is produced also in the same reaction, or it may be the only product if reaction conditions are varied. Other trichloromethyl compounds, such as chloroform and benzotrichloride, react with a fluoroalcohol in the presence of ferric chloride to produce the fluoroalcohol orthoformate and orthobenzoate (cpds V and VI).



Dodecafluoroheptyl
Orthoformate, V



Dodecafluoroheptyl Orthobenzoate,
VI

**PHYSICAL PROPERTIES OF C-5 and C-7
FLUOROALCOHOL CARBONATES AND ORTHOCARBONATES**

Physical testing of the compounds essentially followed existing methods; slight modifications were dictated in some cases by unavailability of sufficiently large samples. The results of fire point, flash point, viscosity, and specific gravity determinations are summarized in Table II. Table III outlines the results of hydrolytic stability and corrosivity tests.

Table II

Compound*	Flash Point** (°F)	Fire Point (°F)	Viscosity, CS		Density g/ml, 60°F
			100°F	210°F	
C-5C=O	350	> 400	7.09	1.52	1.64
C-5OE	415	> 510	35.13	3.84	1.74
C-7C=O	415	> 520	13.64	2.28	1.77
C-7OE	450	> 550	66.42	5.80	1.81
C-7OB					1.82

- * C-5C=O bis(octafluoropentyl) carbonate, $[\text{H}(\text{CF}_2)_4\text{CH}_2\text{O}]_2\text{C}=\text{O}$
 C-5OE octafluoropentyl orthocarbonate, $[\text{H}(\text{CF}_2)_4\text{CH}_2\text{O}]_4\text{C}$
 C-7C=O bis(dodecafluoroheptyl) carbonate, $[\text{H}(\text{CF}_2)_6\text{CH}_2\text{O}]_2\text{C}=\text{O}$
 C-7OE dodecafluoroheptyl orthocarbonate, $[\text{H}(\text{CF}_2)_6\text{CH}_2\text{O}]_4\text{C}$
 C-7OB dodecafluoroheptyl orthobenzoate, $\text{C}_6\text{H}_5\text{C}[\text{OCH}_2(\text{CF}_2)_6\text{H}]_2$

** Tentative values.

Table III
STABILITY-CORROSION DATA ON FLUOROALCOHOL
CARBONATES AND ORTHOCARBONATES¹

Property	Specification Limit	C-7 Orthocarbonate	C-7 Carbonate	C-5 Orthocarbonate	C-5 Carbonate
A. Hydrolytic Stability ²					
1. Copper specimen weight loss mg/cm ²	0.3 mg	0.08 mg	0.36 mg	0.15 mg	0.11 mg
2. Appearance	No visible corrosion	Copper tarnished to a red-violet color; no pitting or corrosion noted at 30 X magnification	Copper tarnished to yellowish color; at 30 X no corrosion noted but specimen had local dark areas	Copper tarnished to yellowish color; at 30 X no dark discolorations, pits or signs of corrosion noted	Copper tarnished to dark brown surface; at 30 X no pits
3. Acidity of water layer mg of KOH	5.0 mg	Solution not acidic	0.84 mg	Solution not acidic	0.84 mg
4. Insolubles		Very slight	Very slight	Very slight	Very slight
B. Copper Strip Corrosion Test ³		Very slight tarnish	Very slight tarnish	Very slight tarnish	Very slight tarnish

¹ C-7 Orthocarbonate = $[\text{H}(\text{CF}_2)_6\text{CH}_2\text{O}]_4\text{C}$, 97.5% pure
 C-7 Carbonate = $[\text{H}(\text{CF}_2)_6\text{CH}_2\text{O}]_2\text{C}=\text{O}$, 98.7% pure
 C-5 Orthocarbonate = $[\text{H}(\text{CF}_2)_4\text{CH}_2\text{O}]_4\text{C}$, 99.9% pure
 C-5 Carbonate = $[\text{H}(\text{CF}_2)_4\text{CH}_2\text{O}]_2\text{C}=\text{O}$, 99.5% pure

² Military Specification MIL-H-19457A (Ships) Amendment 2

³ ASTM Test D130-56

The flash point values obtained by the Cleveland open cup method, ASTM 92, were subject to variation among different operators. Consequently, the temperatures reported in Table II are tentative because of the indefinitiveness of the observed flash point. In addition, the temperature reported for the octafluoropentyl orthocarbonate's flash point, 450°F, is much lower than that reported to us when a small sample was tested for us by Wright-Patterson Air Force Base personnel several months ago. They reported for the C-5 orthoester "no true flash point" up to 500°F and no evidence of thermal instability up to 577°F, the temperature at which the tests ceased.

The density values for the compounds were much higher than expected. All the compounds were heavier than BuShips specifications, possibly reflecting the symmetry of the molecules and relatively high molecular weight. The C-7 fluoroalcohol orthobenzoate was prepared in an effort to ascertain if the density could be lowered by a carbon-hydrogen moiety. However, the dodecafluoroheptyl orthobenzoate density was nearly the same as the orthocarbonate. From this observation it appears that phenyl has the same density effect as the $\text{H}(\text{CF}_2)_6\text{CH}_2\text{O}$ -group.

Corrosivity of the test compounds on copper exposed to the fluids was virtually nil. It was difficult to observe any difference between the copper test specimens and the standard. The results of the hydrolytic stability tests on the fluoroalcohol carbonates and orthocarbonates (summarized in Table III) indicate that these structures are resistant to hydrolysis. With one exception, copper strip weight loss for the C-7 carbonate, the results were well within permissible limits for the military specification MIL-H-19457A (Ships) for phosphate ester. No acidity arose in the orthocarbonate systems, thus confirming the original estimation that the electron withdrawal effect of the fluorine decreased the susceptibility of the orthocarbonate central grouping to hydrolytic action. The titer for acidity in the carbonate hydrolysis corresponds to less than 0.05 percent reaction, indicating that a similar inertness had been imparted to the carbonate group by the electronegativity of the fluorines. For the same reason, inertness toward oxidation would be expected of the carbonate and orthocarbonate groupings.

SYNTHESIS OF FLUOROALCOHOL ORTHOCARBONATES AND CARBONATES

Orthocarbonate Formation

Orthocarbonates were obtained by the reaction of the octafluoropentyl and dodecafluoroheptyl fluoroalcohols with carbon tetrachloride at reflux temperature in the presence of catalytic amounts of anhydrous ferric chloride.



The carbon tetrachloride was used as both reactant and solvent, or alternatively as a reactant added to the alcohol dissolved in chloroform. The reaction system was very sensitive to conditions when carbon tetrachloride was used as solvent; temperature was the most critical variable. Above 78°C the bis carbonates of the fluoroalcohols were formed exclusively, and in all reactions which provided the orthocarbonate the bis carbonate was the principal by-product. Best results were obtained at 76-78°C with little or no orthocarbonate being formed below 76°C. The narrow optimum temperature range presented the practical problem of providing a high heat input because the reaction temperature always dropped when reaction started; possibly this was caused by the cooling effect of hydrogen chloride evolution and solvent entrainment.

The reactant ratios which consistently provided orthocarbonate in 20-42% yields were about 2:1 for carbon tetrachloride to alcohol, and 5:1 for alcohol to anhydrous ferric chloride catalyst. The ratios could be varied somewhat in catalyst quantity without noticeable effect, but greater dilution by additional carbon tetrachloride (already in excess) was detrimental. It was essential to use absolutely anhydrous catalyst, which was easily dried by removing the water from the ferric chloride by the catalyzed hydrolysis of carbon tetrachloride at reflux temperature.¹ The catalyst could be recovered unchanged after the reaction and used again for succeeding experiments.

¹M. E. Hill, J. Org. Chem. 25, 1115 (1960).

In carbon tetrachloride the reaction not only was sensitive to temperature but was apparently affected by the heterogeneity of the system. After about 25-50% of the alcohol had been added, two phases were always present, with catalyst suspended in both phases. In chloroform, the carbon tetrachloride was added stoichiometrically equivalent to the alcohol-chloroform solution and catalyst, giving a reaction system in which the alcohol and the various intermediates were more soluble; homogeneity except for catalyst was maintained. The importance of having reasonable solubility of reactants and intermediates is reflected in the fact that successful reaction in chloroform was obtained at 64°C. Although yields were not improved using chloroform as solvent, results were more reproducible. A small amount of the fluoroalcohol orthoformate was formed in chloroform but its reaction rate was much slower than that of carbon tetrachloride. A good yield of orthoformate required a 93-hour reaction period compared to 6-8 hours for the orthocarbonate synthesis. Ether, nitrobenzene, or 1,2-dichloroethane are not useful as solvents.

In a survey of the scope of the reactions, usable trichloromethyl compounds are confined thus far to carbon tetrachloride, chloroform, and benzotrichloride. Aliphatic trichloromethyl compounds such as 1,1,1-trichloroethane undergo a dehydrohalogenation reaction with anhydrous ferric chloride which forestalls their use in the orthoester reaction. Halogen alcohols, such as the trihydroperfluoropropanol, -pentanol, and -heptanol, and chlorodifluoroethanol all undergo orthoester formation. Normal aliphatic alcohols cause much hydrogen chloride evolution but are not converted to orthocarbonates. Aluminum chloride catalysis produces only the bis carbonate; antimony pentachloride was found to be ineffective.

The preparation of an orthobenzoate can be carried out in chloroform solvent at reflux temperature in about 24 hours. Ether was used successfully as solvent in this reaction, providing the product in 62% yield (some diminution of the catalytic effect of the ferric chloride had been expected). The orthobenzoate formation is accompanied by a side reaction forming the fluoroalcohol benzoate ester.

Proof of Structure

Fractionation of the compounds produced by the reaction of 1H, 1H, 5H-octafluoropentanol with carbon tetrachloride in the anhydrous system gave three principal products which were tentatively identified, in ascending boiling point, as the fluoroalkyl halide, the bis fluoroalkyl carbonate, and a possible orthocarbonate. Infrared analysis of the proposed orthocarbonate was similar to the spectrum of a perfluoroalkyl group, providing evidence only for the absence of hydroxyl and carbonyl groups or other functional groups. Element analysis for carbon and hydrogen gave values almost the same as contained in the parent alcohol, suggesting that the alcohol did not undergo appreciable change. A calculated empirical formula did not permit a choice between possible self-condensation of the alcohol or reaction with carbon tetrachloride to form the orthocarbonate or orthoformate. However, nuclear magnetic resonance spectra of the products gave proton spectra expected for the $-CF_2H$, with a τ value of 4.05 for the proton peak, which was split into a triplet by the two fluorine atoms on the same carbon and split again by the $\beta-CF_2$ group. The methylene moiety was a triplet at τ 5.78 whose integrated peak area ratio to the HCF_2 -proton was very close to the calculated ratio of 2 to 1. Consequently the alcohol moiety had not undergone reaction at the terminal HCF_2 -position, and the requisite proton arrangement for an orthocarbonate was present in the molecule. Finally, the molecular weight of the trihydroperfluoropentanol product was within 3% of the calculated value, 967 found versus 936 calculated, for an orthocarbonate. A similar result was obtained in the molecular weight determination of the orthocarbonate of trihydroperfluoroheptanol. The molecular weight measurements, coupled with the nuclear magnetic resonance spectra and elemental analyses, was considered to be sufficient evidence to assign the orthocarbonate structure to the highest boiling of the products of the reaction.

Confirmatory evidence for orthoester formation from trichloromethyl compounds was provided by the synthesis of the corollary trihydroperfluoroheptyl orthoformate, and orthobenzoate. The nuclear magnetic resonance proton spectra of these compounds had the requisite

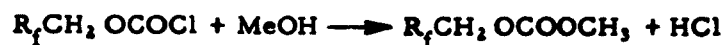
peaks and integrated peak area ratio for the ortho structures. Furthermore, the infrared spectra and elemental analyses provided supporting data for the orthoformate and orthobenzoate structural assignment.

Bis Carbonate Formation

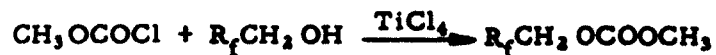
The reaction producing the orthocarbonate was always accompanied by the formation of the bis carbonate, $(R_fCH_2O)_2C=O$, as a by-product. Originally the carbonate was thought to arise from the hydrolysis of the possible intermediate, $(R_fCH_2O)_2CCl_2$, during workup which involved an aqueous wash to remove ferric chloride. However, the carbonate was isolated directly from the reaction mixture in an experiment which employed strictly anhydrous conditions. In addition to the carbonate, a new compound which analyzed as the trihydroperfluoroalkyl halide was also isolated. The formation of the carbonate under anhydrous conditions indicated that the carbonyl oxygen of the carbonate came from the alcohol in some manner.

In a variation of the original "wet" system (to obtain in situ formation of the carbonate) water was added to the carbon tetrachloride-fluoroalcohol-ferric chloride system in order to hydrolyze the proposed dialkoxydichloromethane intermediate. In addition to the bis carbonate, a new compound was isolated. The new product was relatively low boiling, and reacted with water, giving a solution which produced positive test for chlorine. The infrared spectrum showed the presence of carbonyl. On the basis of this evidence the compound was assigned a fluoroalcohol chlorocarbonate structure, which was later verified experimentally. This method provides the first example of a chlorocarbonate being prepared in such a manner.

The chlorocarbonate reacted vigorously with methanol to produce methyl trihydroperfluoropentyl carbonate.



The mixed carbonate was independently synthesized from methyl chlorocarbonate and the fluoroalcohol using metal halide catalysis:²



The two products were identical in all respects, thereby confirming the assignment of the chlorocarbonate structure to the new compound obtained from the carbon tetrachloride-alcohol-water-catalyst system.

With titanium tetrachloride as catalyst, the octafluoropentyl chlorocarbonate was converted to a "mixed" fluoroalcohol carbonate by reaction with dodecafluoroheptyl alcohol.



This compound has a boiling point of 85°C/0.2 mm.

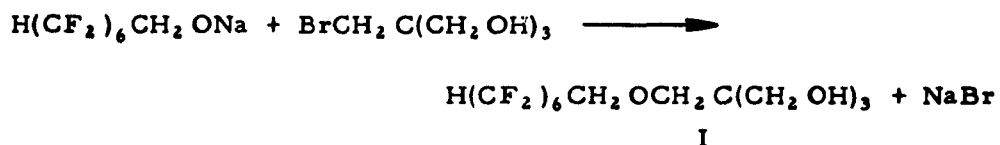
²M. E. Hill, J. Am. Chem. Soc., 76, 2329 (1954).

MISCELLANEOUS REACTIONS

In a brief study of the scope of the catalyzed condensation of carbon tetrachloride with "active hydrogen" compounds, an experiment with chlorobenzene was run. A product was obtained which was a mixture of a badly discolored intractable oil and p,p'-dichlorodiphenyl. Further identification of the oil was not attempted.

Two more highly fluorinated alcohols, $\text{H}(\text{CF}_2)_8\text{CH}_2\text{OH}$ and $\text{H}(\text{CF}_2)_{10}\text{CH}_2\text{OH}$, were used in the orthocarbonate reaction to determine if their orthocarbonates would be very high boiling liquids. The C-9 fluoroalcohol gave only the bis carbonate from carbon tetrachloride in chloroform solvent, and did not react at all in ether. No reaction was obtained with the C-11 fluoroalcohol in chloroform, possibly because of the alcohol's solubility in the solvent.

An approach to the preparation of a new series of water-soluble fluids was briefly explored by the preparation of the C-7 fluoroalcohol ether of pentaerythritol.



The C-7 fluoroalcohol sodium alkoxide was prepared by the alcoholysis of sodium methoxide by C-7 fluoroalcohol. Bromopentaerythritol was prepared by a preparation described in the open literature. The reaction of the bromo compound and fluoroalcohol alkoxide was carried out at room temperature for 50 hours, using the fluoroalcohol as solvent. Analysis of the reaction mixture by gas chromatography showed that at least two products had been formed in low yield. These products were tentatively considered to be the pentaerythritol monomethyl ether and the desired product, C-7 fluoroalkyl ether, I. Study of this reaction was discontinued because of the low yields.

EXPERIMENTAL

The trihydroperfluoro alcohols were obtained from the duPont de Nemours Company. The ferric chloride was commercial sublimed anhydrous grade, re-dried before each experiment by refluxing in carbon tetrachloride for at least 16 hours.

The following procedures are exemplary of the general methods used to prepare orthocarbonates which are summarized in Table IV. Nuclear magnetic resonance data are summarized in Table V.

Table IV

FLUOROALCOHOL ORTHOESTERS AND CARBONATES

Compound	B. P. (°C/ mm)	% Yield (Solvent)
1H, 1H, 7H-Dodecafluoroheptyl		
Orthocarbonate	170°/0.008	35 (CCl ₄) 35 (CHCl ₃)
Orthobenzoate	187°/1.0	28 (CHCl ₃) 62 (Ether)
Orthoformate	139°/0.1	80 (CHCl ₃)
Carbonate	99°/0.01	48 (CCl ₄) 42 (CHCl ₃)
1H, 1H, 5H-Octafluoropentyl		
Orthocarbonate	135°/0.003	42 (CCl ₄)
Carbonate	98°/0.005	36 (CCl ₄)

Table V
NUCLEAR MAGNETIC RESONANCE DATA ON ORTHOESTERS

<u>Assignment</u>	<u>τ Value</u>	<u>Splitting</u>	<u>J Value, cps</u>
<u>$[\text{H}(\text{CF}_2)_6\text{CH}_2\text{O}]_4\text{C}$</u>			
-CH ₂ -	5.78	Triplet	12.0
-CF ₂ H	4.05	Triplet	48.2
		Triplet, α -CF ₂	5.1
<u>$[\text{H}(\text{CF}_2)_6\text{CH}_2\text{O}]_3\text{CC}_6\text{H}_5$</u>			
-CH ₂ -	5.97	Triplet	12.0
HCF ₂ -	4.05	Triplet	48.5
		Triplet, α -CF ₂	4.5
Phenyl	2.50	Singlet	--
<u>$[\text{H}(\text{CF}_2)_6\text{CH}_2\text{O}]_3\text{CH}$</u>			
-CH ₂ -	5.76	Triplet	12.2
HCF ₂ -	4.07	Triplet	47.8
		Triplet, α -CF ₂	4.9
HC	4.18	Singlet	--
<u>$[\text{H}(\text{CF}_2)_6\text{CH}_2\text{O}]_2\text{C=O}$</u>			
-CH ₂ -	5.32	Triplet	13.2
HCF ₂	3.99	Triplet	51.2
		Triplet, α -CF ₂	6.0

1H, 1H, 7H-Dodecafluoroheptyl Orthocarbonate

Method A

To a vigorously stirring mixture of 16 g (0.01 mole) of anhydrous ferric chloride in 75 ml of carbon tetrachloride at reflux temperature, 83 g (0.25 mole) of 1H, 1H, 7H-dodecafluoroheptanol was added dropwise over a period of 2.5 hours. The heat input from the heating mantle was adjusted to maintain the temperature of the reaction at 76-78°C. After the addition of the alcohol, heating was continued until hydrogen chloride evolution was very slow (6 hrs). The ferric chloride was filtered from the dark-colored reaction mixture, and the reaction solution was dissolved in ether, washed several times with water, and dried. The solvents were removed at 20-35 mm pressure, leaving a dark viscous oil. The oily product was fractionated, yielding 40 g (48%) of bis (1H, 1H, 7H-dodecafluoroheptyl)carbonate, b.p. 99°/0.01 mm, and 28 g (35%) of 1H, 1H, 7H-dodecafluoroheptyl orthocarbonate, b.p. 170°/0.008 mm. Refractionation of foreruns produced 9.8 g, b.p. 145°/760 mm, of the alcohol halide, identified by NMR, infrared, and elemental analyses.

Method B

Carbon tetrachloride (10.4 g, 0.067 mole) was added over a period of 30 minutes to a refluxing mixture of 11 g (0.06 mole) of ferric chloride and a solution of 66 g (0.20 mole) of 1H, 1H, 7H-dodecafluoroheptanol in 100 ml of chloroform. The reaction mixture was held at reflux temperature an additional 5 hours, cooled, filtered, and dissolved in ether. The ether solution was washed several times with water, separated, dried, and evaporated to an oily residue. Fractionation of the crude product yielded 23 g (35%) of the orthocarbonate, 28 g (42%) of the bis carbonate, and 6.0 g (9%) of the alkyl halide.

1H, 1H, 7H-Dodecafluoroheptyl Orthoformate

A mixture of 83 g (0.25 mole) of 1H, 1H, 7H-dodecafluoroheptanol, 120 g of chloroform (1 mole), and 22 g of anhydrous ferric chloride was held at reflux temperature for 93 hours. After cooling and filtering,

the dark reaction solution was distilled at reduced pressure. The orthoformate (58 g) was obtained at 137-139°/0.1 mm in 80% yield.

1H, 1H, 7H-Dodecafluoroheptyl Orthobenzoate

To a solution of 350 ml of dry diethyl ether and 695 g (2.1 moles) of 1H, 1H, 7H-dodecafluoroheptanol mixed with 44 g ferric chloride, 136 g (0.7 mole) of benzotrichloride was added dropwise at 50°C over a period of 1-1/4 hours. The reaction mixture was heated until the hydrogen chloride evolution was virtually nil (16 hours) and then mixed with 500 ml of water. The ether layer was separated, washed with water, dried over magnesium sulfate, and evaporated to an oily residue under reduced pressure. Fractionation of the crude product produced recovered alcohol, 198 g of fluoroalcohol benzoate, b.p. 155°/0.5 mm, and 295 g of 1H, 1H, 7H-dodecafluoroheptyl orthobenzoate, b.p. 187°/0.1 mm, 62% yield based on unrecovered alcohol.

1H, 1H, 5H-Octafluoropentyl Chlorocarbonate

A solution of 69.6 g (0.3 mole) of 1H, 1H, 5H-octafluoropentanol and 5.4 g (0.3 mole) of water was added intermittently over a period of 1-1/4 hours to a mixture of 26.4 g of ferric chloride in 60 ml of carbon tetrachloride at 76°C. Large amounts of phosgene and hydrogen chloride were evolved over a period of 5 hours and the reaction was allowed to continue an additional 12 hours. After cooling, the entire reaction mixture was dissolved in ether, washed very quickly with cold water, dried, and distilled. The fractionation gave 10 g of recovered alcohol, 20 g (30%) of the chlorocarbonate, b.p. 33°/0.4 mm, and 31 g (42%) of the bis carbonate.

A part of the chlorocarbonate (6.0 g, 0.02 mole) was added to excess methanol in ether at 50°C. Distillation after workup yielded 4.3 g (70%) of methyl 1H, 1H, 5H-dodecafluoropentyl carbonate, b.p. 50°/0.15 mm.

Methyl chlorocarbonate (10.4 g, 0.11 mole) was stirred with 23.2 g (0.1 mole) of 1H, 1H, 5H-octafluoropentanol in chloroform

containing 0.02 mole of titanium tetrachloride for 5 hours at 50°C. After workup similar to above experiments, fractionation of the product yielded 24.2 g (80%) of the methyl fluoroalcohol carbonate, b. p. 46°/0.1 mm.

The two methyl fluoroalcohol carbonates from these experiments were found to be identical by infrared analysis and by determination of the same retention times by GLPC.

1H, 1H, 5H-Octafluoropentyl -- 1H, 1H, 7H-Dodecafluoroheptyl Carbonate

A solution of 15.5 g (0.0526 mole) of octafluoropentyl chloro-carbonate, 18.1 g (0.0545 mole) of dodecafluoroheptanol, and 2.4 g of titanium tetrachloride in 45 ml of chloroform was heated at reflux temperature for 2 hours. After cooling, the solution was washed with 50 ml of cold 0.5 hydrochloric acid, separated, and dried with calcium sulfate. The solvent was stripped from the crude product, which was fractionated. The mixed carbonate was obtained in 80% yield at 85°C/0.02 mm.

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